

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
<small>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small>				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 9/23/97	3. REPORT TYPE AND DATES COVERED Final Technical Report 6/1/93-5/31/97	
4. TITLE AND SUBTITLE Fundamental Studies of a High Energy Molecular System			5. FUNDING NUMBERS F49620-93-1-0326 PARENT GRANT 61102F 2303 ES F49620-92-J-0573 61103-D 3484/XS	
6. AUTHOR(S) Mitchio Okumura				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Chemistry Department 127-72 California Institute of Technology 1200 East California Blvd. Pasadena, CA 91125			8. PERFORMING ORGANIZATION REPORT NUMBER AFOSR TR 97-0414	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Dr. Michael Berman, Program Manager AFOSR/NL 110 Duncan Avenue, Suite B115 Bolling AFB DC 20332-0001			10. SPONSORING/MONITORING AGENCY REPORT NUMBER F49620-93-1-0326	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.			12b. DISTRIBUTION CODE <div style="border: 1px solid black; padding: 5px; text-align: center;"> DISTRIBUTION STATEMENT A Approved for public release Distribution Unlimited </div>	
13. ABSTRACT (Maximum 200 words) <p>Metal-atom-doped solid hydrogen has shown promise as a High Energy Density Material with greatly improved propulsion properties; however, the production of high concentrations of atoms in a cryogenic medium has been highly problematic. The objective of this contract was to investigate at a fundamental level the intermolecular forces which determine the structure and properties of the dopant atoms in the host matrix. Aluminum atoms in argon clusters provided a model system with which to test theoretical methods being developed at Phillips Laboratory, Edwards AFB. Spectroscopic measurements of these clusters were performed on a new spectrometer developed under the parent contract. Comparisons of the observations with theoretical calculations revealed the inadequacies of many common assumptions and demonstrated the importance of the mixing of electronic states of the atoms in the presence of the perturbing cluster or matrix. These results provided a benchmark for theory and yield important insights into the interpretation of the electronic spectra of doped matrices.</p>				
14. SUBJECT TERMS			15. NUMBER OF PAGES 32	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT u	18. SECURITY CLASSIFICATION OF THIS PAGE u	19. SECURITY CLASSIFICATION OF ABSTRACT u	20. LIMITATION OF ABSTRACT u	

Fundamental Studies of a High Energy System

AASERT Award
June 1, 1993 to May 31, 1997
Final Technical Report
AFOSR Contract F49620-93-1-0326

TO: Dr. Michael Berman
AFOSR NL
110 Duncan Avenue
Bolling AFB, DC 20332

FROM: Mitchio Okumura
*Arthur Amos Noyes Laboratory of Chemical Physics
Mail Code 127-72
California Institute of Technology
1200 East California Blvd.
Pasadena, CA 91125*

SUMMARY

Light atom-doped solid hydrogen has been under investigation as a candidate High Energy Density Matter (HEDM) propellant with prospects of improved specific impulse.^{1,2} One objective of the HEDM program has been to simulate the properties of such systems using state-of-the-art theoretical methods. Experimental studies of small clusters provide important results against which to test theory, by providing both data on two-body intermolecular potentials and size-dependent trends in relatively small, tractable systems.

In the work described here, we have investigated the electronic spectroscopy of AlAr_n clusters, with $n = 1$ to 54. Through direct collaboration with theorists at Edwards AFB, we have benchmarked theoretical methods being developed for modeling HEDM material. Our results provide benchmarks for calculations of excited state potentials of AlAr ; more

important, they test simulation results using computational code based on the Spectral Theory. Comparison of theory and experiment test the validity of common assumptions made in modeling the electronic spectra of matrix-isolated metal atoms and seem to reveal the importance of configuration mixing in such systems.

1. Instrument Development and Cryogenic Laser Ablation Source

The students supported by this AASERT award assisted in constructing the molecular beam machine funded by the parent grant. Much of the additional effort focused on the design and fabrication of several new versions of a piezo-driven pulsed-valve laser ablation source. Specific innovations developed under this contract included design for use at cryogenic temperatures, and modifications to handle soft and reactive metals. This source was intended for use in generating weakly bound adducts such as B-H₂. Metal atoms were generated by laser ablation into the expansion of a low temperature gas.

2. Spectroscopy of AlAr_n Clusters

We investigated the evolution of the electronic spectra of Al atoms doped in larger Ar clusters. Our object was to use cluster spectra as a probe of how metal atoms interacted with inert gas hosts. Resonant multiphoton ionization spectra were recorded in the 3p → 3d and 3p → 4p spectral regions of AlAr_n for $n \geq 55$. The spectra exhibited splittings and shifts which differed in significant ways from the spectrum of Al atoms doped in matrices.

The current results provided a benchmark for theoretical studies underway at Edwards AFB using methods being developed to predict the properties of metal atom-doped solid hydrogen. Our results were compared directly to calculations by Boatz and Sheehy using both the Balling and Wright model³ and Langhoff's Spectral Theory.⁴ These comparisons

19971006 013

DTIC QUALITY INSPECTED 3

provided insights into the cluster structure as well as the electronic states of the aluminum atom within the cluster.

3. Observation of New States of AlAr

Spectra were recorded of the diatomic molecule AlAr by resonant multiphoton ionization spectroscopy in the $3p \rightarrow 3d$ and $3p \rightarrow 4p$ spectral regions. We observed new spectra detectable only by two photon absorption from the ground state. We assigned the spectra to excitation of molecular Σ and Π states arising from the $4p$ state of atomic Al. We also observed new bands in the $(3d)^2\Delta$ state which indicate that the literature value of the origin is incorrect.

Our studies provided clear evidence of state mixing among states arising from both the $3d$ and $4p$ atomic states. These spectra were compared to high level MCSCF calculations of the diatomic potential energy curves performed by Dr. Jeff Sheehy. The experimental results obtained in this grant suggested that refinements and adjustments to the calculations were necessary to correctly describe the perturbations.

4. Spectra of Al-Adducts

We searched for spectra of other weakly bound adducts, including $\text{Al}(\text{H}_2\text{O})$ and AlNe . No definitive assignment was made of the observed spectra. The data are compiled in the thesis of M. S. Johnson (Ph.D., Caltech, 1995, see below).

5. Personnel Participating in Research:

- a. Principal Investigator: Mitchio Okumura
- b. Graduate Students: Matthew S. Johnson
James Michael Spotts
Keith T. Kuwata

C. Undergraduates: Carolyn Cohran (Minority Undergraduate Research Fellow)

Gary T. Olsen

6. Ph.D. Thesis:

Matthew S. Johnson, 1995. "Spectroscopy of Reactive Molecules and Clusters"

California Institute of Technology.

This thesis presents detailed construction of the laser-induced fluorescence apparatus and details preliminary results on the putative spectroscopy of $\text{Al}(\text{H}_2\text{O})$. A tentative assignment of the progressions observed near 300 nm is presented. This thesis can be obtained through the

Department of Chemistry 164-30

California Institute of Technology

1200 E. California Blvd.

Pasadena, CA 91125

as well as the Xerox Microfilm Library.

MOTIVATION AND AIR FORCE INTERESTS

The High Energy Density Matter (HEDM) program has identified atom-doped solid hydrogen as a high energy molecular system with promise as an alternative rocket propellant that can provide significant improvements in specific impulse (I_{sp}) over conventional propulsion technology. Calculations indicate that doping of light metal atoms as well as their dimers can yield increases in I_{sp} 's of several percent at reasonable doping concentrations. Critical issues in scaleup and engineering remain to be addressed. Modeling of the structure and dynamics of these systems at the molecular level provide a fundamental basis for efforts to develop these materials as viable propellant systems.

Matrix spectroscopy is one of the most important probes of the physical environment around a dopant atom. A key uncertainty in matrix studies underway at Phillips Laboratory, Edwards AFB, lies in the interpretation of the matrix-induced shifts and splittings of atomic spectral transitions. Such experiments must ultimately rely on high level calculations to correctly predict the splittings and shifts expected. The theory must accurately compute two properties: the structure of the matrix and the perturbations induced by the matrix on the electronic spectrum of the dopant atom. Additional uncertainties such as multiple trapping sites further complicate the analysis of matrix spectra.

High resolution spectroscopy of clusters provides a far simpler means of exploring the potential energy surfaces that govern the dynamics in the condensed phase. The intermolecular forces in solid hydrogen and in inert rare gas matrices are weak and can be precisely probed in spectroscopic studies of small clusters of a single dopant atom (or molecule) complexed with inert rare gas atoms (e.g. Ar) and H_2 molecules. Furthermore,

the small size of the systems provides a relatively tractable system for theoretical modeling. Investigations of clusters can thus provide detailed information concerning the interaction between a metal dopant and the surrounding hosts, the fundamental data necessary to accurately model the behavior of a guest dopant metal with a surrounding host hydrogen matrix. Most importantly, the results of specific cluster studies also serve as rigorous tests of the theoretical methods that are being developed at Phillips Laboratory to calculate the properties of solid H_2 and other HEDM material.

Our goal has been to investigate the spectroscopy of clusters in order to understand the guest-host interactions that exists between metal atoms doped in solid molecular and atomic matrices and the surrounding host atoms/molecules. Two sets of experiments have been initiated. In the first, spectroscopic studies have been performed at Caltech to address directly the issue of how the electronic transitions of atoms bound to clusters and the cluster structure around the dopant evolve as a function of cluster size; these experiments have focused on a model system $Al(Ar)_n$. In the second, higher resolution spectra were recorded of the diatomic $AlAr$ molecule. These experiments were undertaken to observe previously undetected excited states arising from the 4p atomic state of Al via two photon transitions from the ground state.

MULTIPHOTON IONIZATION APPARATUS

A schematic of the apparatus constructed during this performance period is shown in Figure 1. It consists of a vacuum chamber with three stages of differential pumping. Region 1 is pumped by two baffled VHS-10 diffusion pumps; region 2 is pumped by a cryotrapped VHS-6 diffusion pump. Region 3 has provisions for additional pumping but is currently not differentially pumped.

In the first chamber is the molecular beam source, a piezo-electric-driven pulsed valve utilizing laser ablation to introduce atoms into the expanding jet of gas. Clusters are formed in the ensuing supersonic expansion.

The UV probe laser can be introduced into either region 1 or region 2 for spectroscopic studies. Region 1 contains the optics for collecting laser-induced fluorescence. For photoionization experiments, the expansion is collimated by a 3 mm skimmer. The beam is ionized by photons from a YAG-pumped dye laser (Continuum NY-61 pumping a TDL-51 dye laser). The dye laser output can be doubled or mixed to generate ultraviolet radiation with 1-10 mJ of energy depending on wavelength. Photoions are extracted with ion optics configured in a Wiley-McLaren design.⁵

Region 3 contains the 1-m flight path of the time-of-flight mass spectrometer and Galileo FTD-2003 microchannel plate detector. A mass-gate has also been installed to allow for gating the mass of interest. TOF mass spectra were collected by a transient digitizer (LeCroy 8818). Individual scans were recorded by gating the mass peak of interest with a gated integrator. Both LIF and photoionization spectra were recorded with dual gated integrators (Stanford Research Systems). All spectra were normalized for laser fluence.

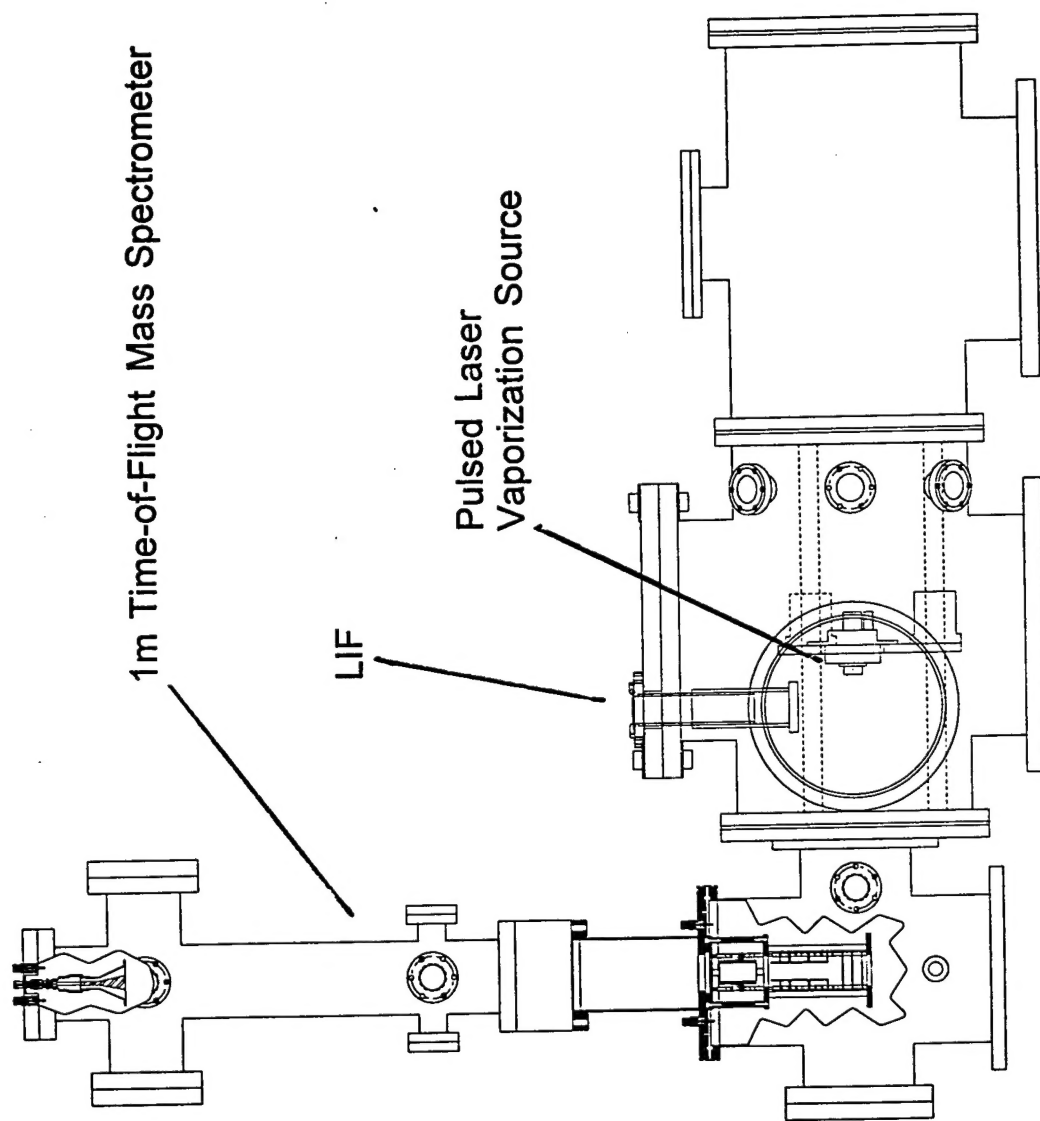


Figure 1. Photoionization/Laser -induced fluorescence spectroscopy apparatus.

LASER ABLATION SOURCES

A pulse of gas, typically 100 to 200 μs in duration, was formed with a piezo-electric-driven pulsed valve based on the design of Proch and Trichl (see Figure 2).⁶ Clusters such as $\text{Al}(\text{Ar})_n$ were generated by laser vaporization of a target rod at 355 nm (from a tripled Continuum Surelite II Nd:YAG laser) near the exit region of the source with clustering of carrier gas to the metal atoms occurring during the ensuing supersonic expansion.

We experimented with several versions of the nozzle/vaporization geometry, as illustrated in Figures 2 through 4. A balance is needed between the high pressure conditions needed for cluster formation and the need to maximize atomic Al (as opposed to higher metal clusters Al_n). Most of the experiments performed used the nozzle shown in Figure 2.

Figure 4 illustrates a modification which allowed us to cool the laser vaporization region to cryogenic temperatures (77 K) using a nozzle extension, following similar adaptations built at Berkeley.⁷ The piezo-electric element can only operate at temperatures above 273 K. To cool the nozzle further, the shaft and body were extended approximately 8 cm from the piezo-element. The seal was made with a Kel-F tip pressed against a highly polished surface. The main body of the source could thus be kept at room temperature, with the tip (and hence final stagnation volume) cooled to 77 K. The extension provided a long distance over which a thermal gradient could be established.

We redesigned the laser vaporization source to allow us to handle softer metals such as lithium and sodium. To do so, we had to modify the metal support system to support the rod without leading to excessive deformation of the metal. We chose to use a cart design, using rods and bearings. This source is shown in Figure 4.

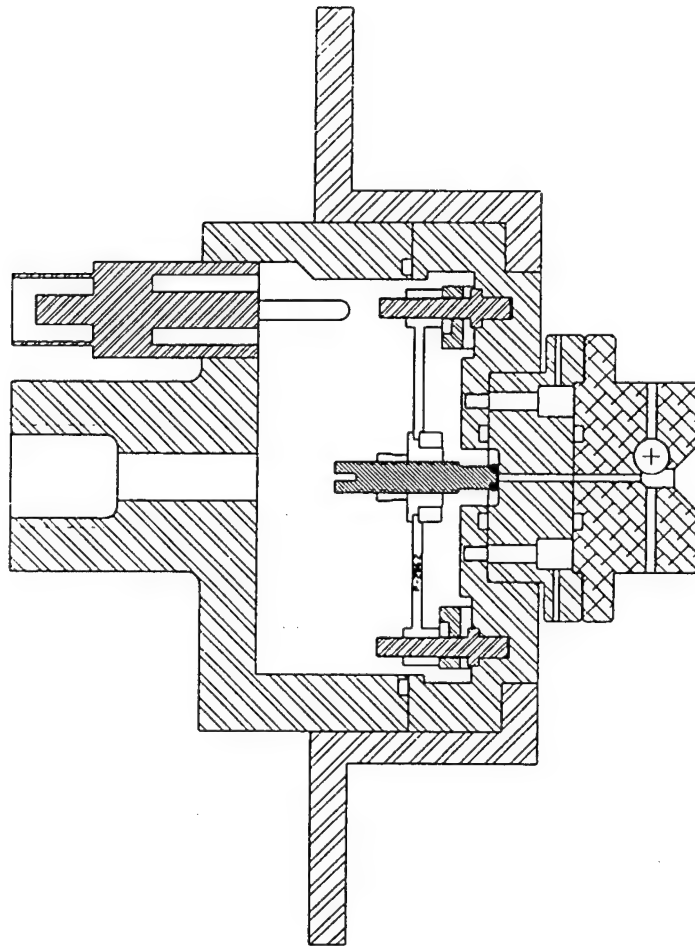


Figure 2. Pulsed valve with laser vaporization assembly.

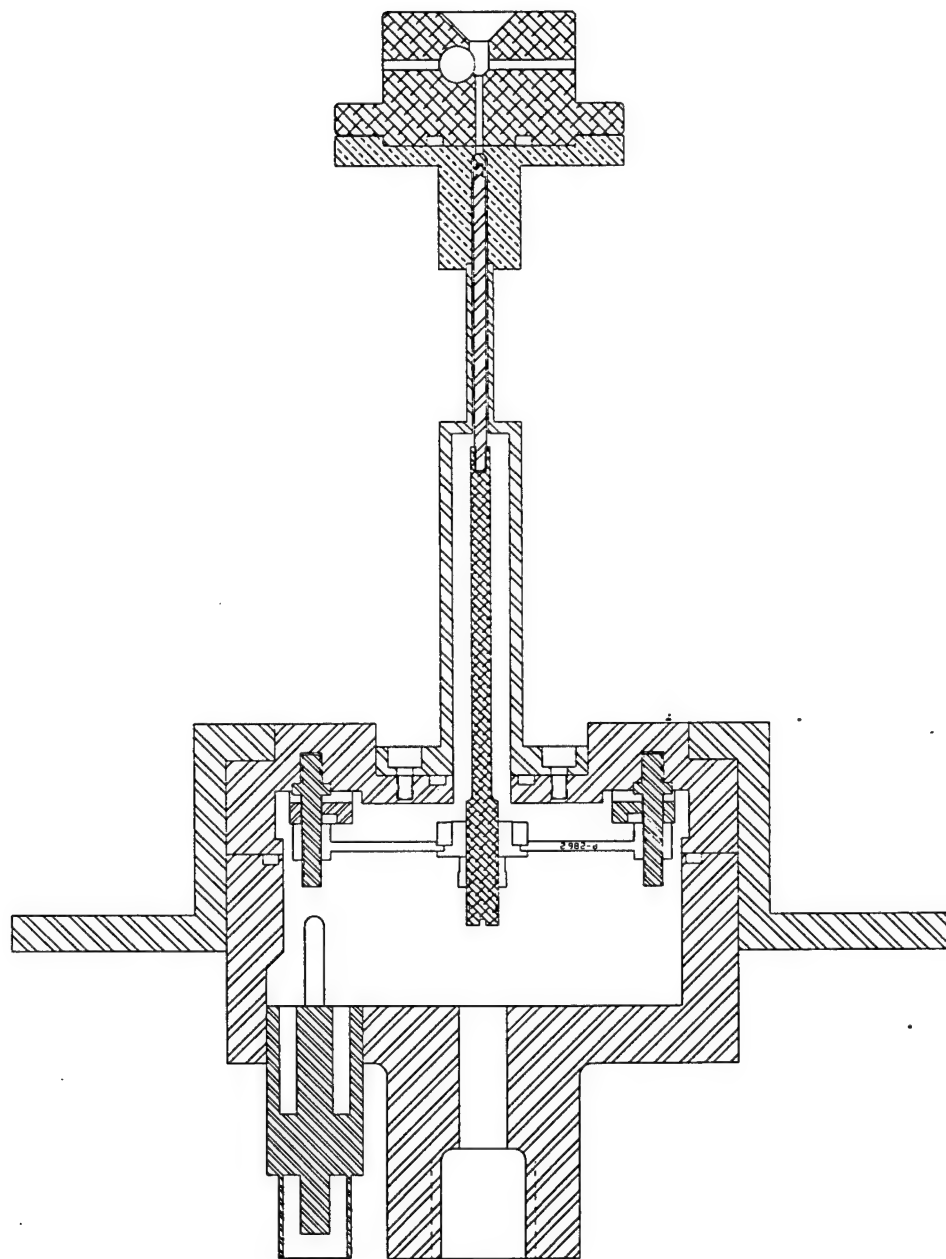


Figure 3. Cryogenically cooled pulsed valve/laser vaporization source.

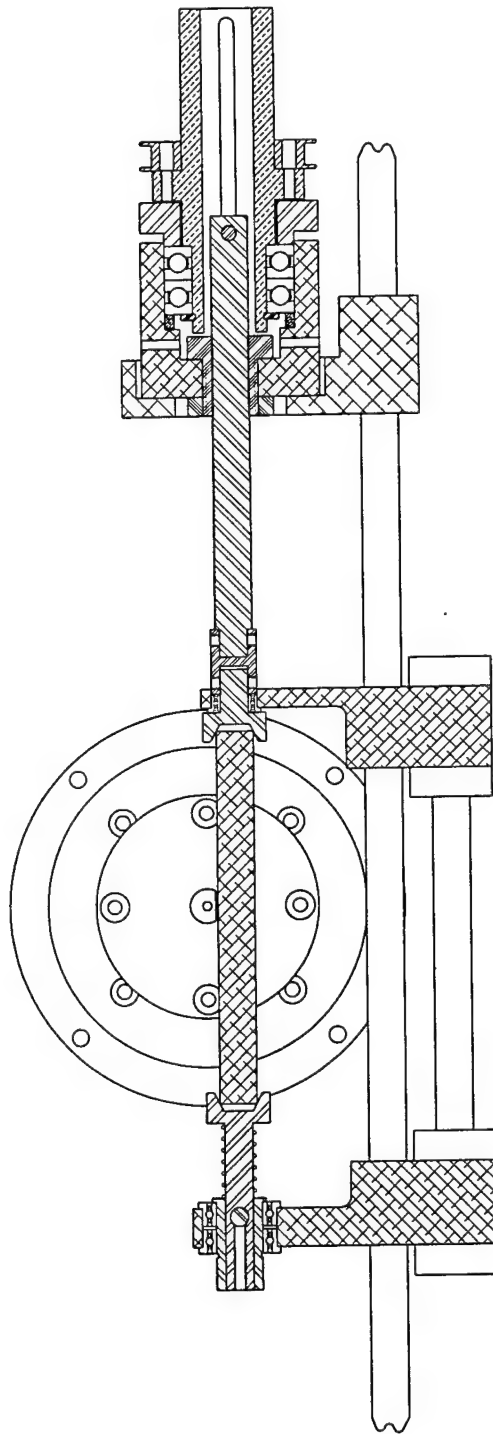


Figure 4

EXPERIMENTAL METHODS

All of the spectra reported here were obtained by one- or two-color multiphoton ionization of AlAr_n clusters. The experiment was performed on the time-of-flight mass spectrometer described earlier. $\text{Al}(\text{Ar})_n$ clusters were generated by a standard laser vaporization techniques. Following the opening of a piezoelectric pulsed valve, the pure Ar carrier gas (~ 8 atm. stagnation pressure) entered the first of three regions of the laser vaporization source (Figure 1 of Section II). The first region consisted of a 0.040" \varnothing channel that then opened up at 10° in region 2 to join region 3, a straight $\varnothing 0.100$ " channel. The tripled output of a Nd-YAG laser (Continuum Surelite 1) was focused on the surface of a rotatable 2024 Al rod that was positioned 0.105" after region 2. Following supersonic expansion, the clusters passed through a 3-mm skimmer into the second differential region. The clusters were then ionized by 1+1' or 2+1' resonant one- or two-color multiphoton ionization by crossing the jet with an unfocused pump beam consisting of both the residual fundamental and doubled fundamental of the appropriate laser dye wavelength (DCM, Rhodamine 640/610). The pump laser was the output of a dye laser (Quintel TDL-51) pumped by a Nd:YAG laser (Continuum NY-61) that was doubled to generate the UV beam (1-4 mJ/pulse).

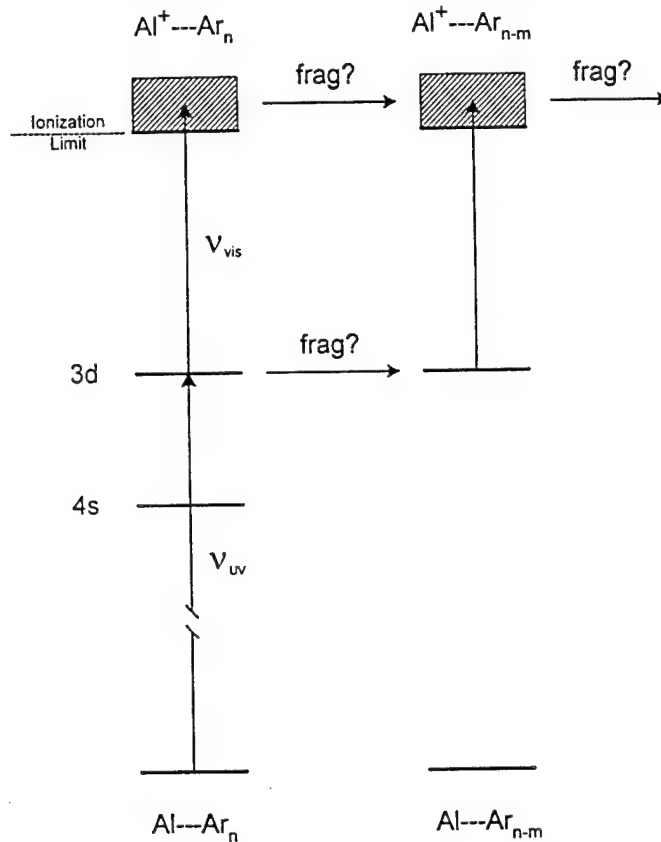
Following ionization, the clusters were extracted perpendicularly and mass-analyzed by a standard 1-m Wiley-McLaren time-of-flight (TOF) spectrometer, and detected by a microchannel plate. TOF mass spectra (Figure 5) were collected by a transient digitizer (LeCroy 8818). Individual scans were recorded by gating the mass peak of interest with a gated integrator. S/N was greatly improved by switching the laser vaporization Q-switch at half the rep rate and using the gated integrator to subtract the pump background due to

DP oil contaminant fragments (LV off) from every signal shot (LV on). All spectra were normalized for UV fluence.

Figure 5 shows the ionization scheme employed for the 1+1' MPI experiments. In the UV excitation (first step) experiments, the laser was scanned through the UV region from 330 nm to 296 nm, first exciting the Al atom $3p \rightarrow 3d$ transition with the doubled UV photon, and subsequently ionizing with the visible fundamental dye photon (10-50 mJ/pulse). In the current single dye laser experiments, the UV and visible wavelengths ($\nu_{\text{vis}} = \frac{1}{2}\nu_{\text{UV}}$) were forced to tune simultaneously. The total photon energy ($\nu_{\text{UV}} + \nu_{\text{vis}}$) was always within 0.75 eV or less of the ionization threshold of the clusters.⁸

The two photon absorption spectra were recorded in a similar manner. These were then 2+1' MPI measurements, with two photons required to excite the resonance and were performed with one color, the visible (direct laser) output.

Resonant Multiphoton Ionization Scheme for AlAr_n



Typical T.O.F. Mass Spectrum

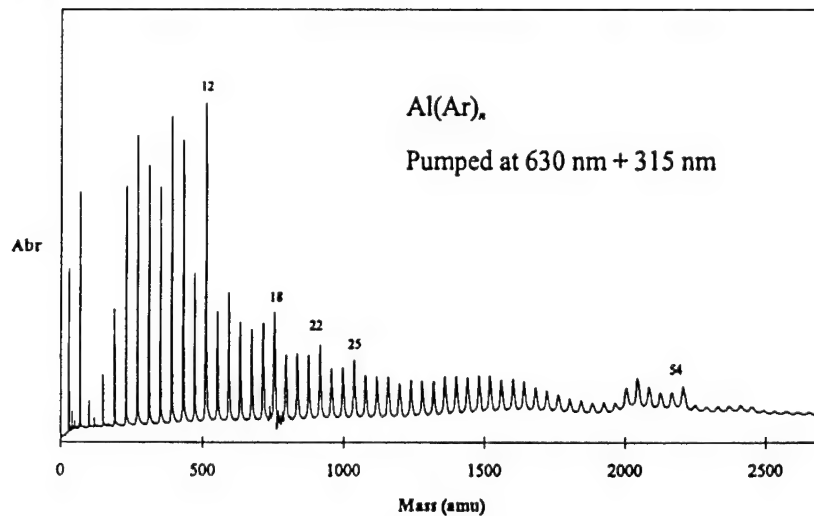


Figure 5

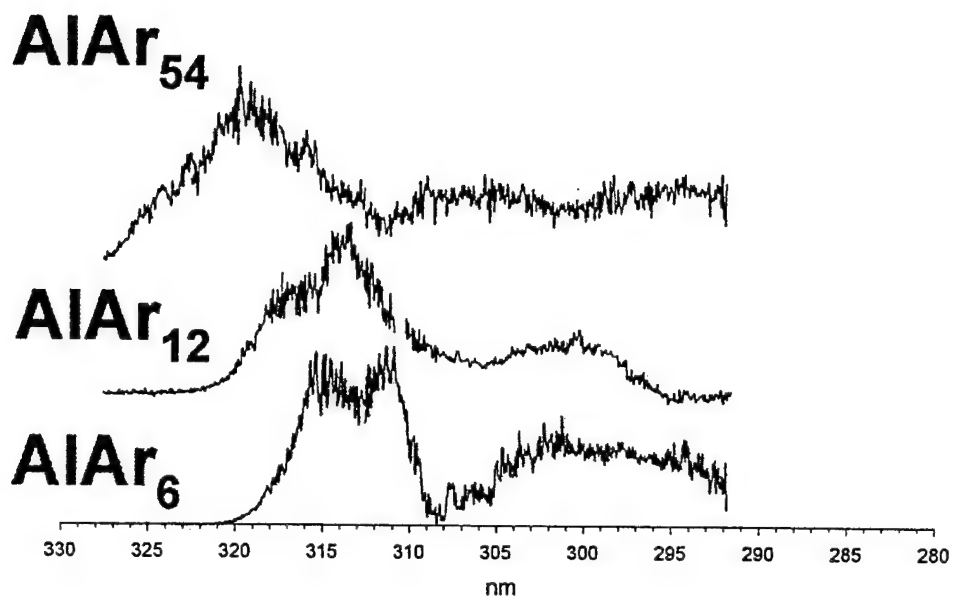
SPECTROSCOPY OF THE 3d/4p STATES OF Al ATOMS IN AlAr_n CLUSTERS

UV spectra of Al(Ar)_n clusters were taken by 1+1' multiphoton ionization over the wavelength range from 292 nm to 328 nm. At any given wavelength, the ionization photon was half the energy of the UV photon. Spectra of three representative clusters are shown in Figure 6. Additional spectra are given in the Final Technical Report of the parent contract. All of the clusters ($n = 4 - 54$) exhibited two broad principal transitions. We have tentatively assigned them as arising from the Al 3p→3d transitions. In each case, one band was blue-shifted relative to atomic Al 3p→3d transition (308.215 nm), and the other red-shifted. Some structure was often evident but no sharp features were ever resolved.

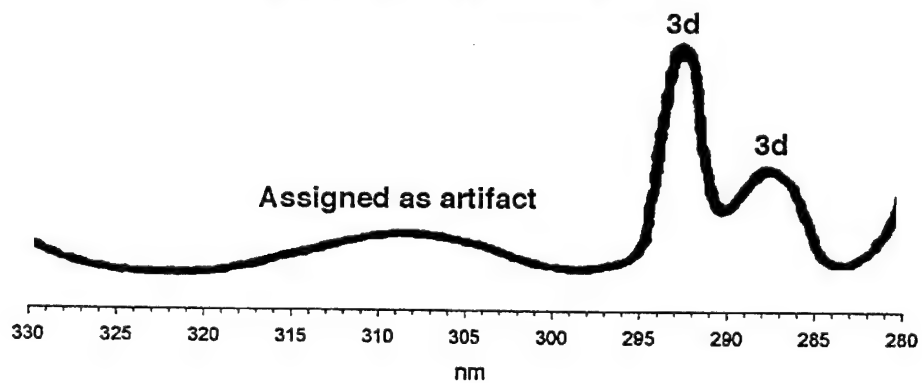
The blue-shifted bands were generally broad and asymmetric. For smaller clusters ($n \leq 12$), the peak shifted to the blue as n increased. However, a splitting was observed for larger clusters ($n \geq 18$). At $n = 18$, the peak was more symmetric and a dip started to appear at around 301 nm. The splitting became more pronounced as n increased.

The red-shifted bands were observed in the 325-308 nm region. The peaks were also broad and asymmetric, but they showed a monotonic increase in the red-shift relative to the atomic transition with cluster size. Moreover, the band positions varied in a stepwise fashion with n , and the changes appeared to coincide with the shell sizes ($n = 12$, and 54) for icosahedral shell closings.^{7,9} As shown in Figure 6, the peaks were close to 312 nm for $n \leq 12$, 320 nm for $25 \leq n \leq 40$, and 324 nm at $n = 54$. This result suggested that the observed spectral shifts indeed reflected the structural evolution in the clusters, and that cluster fragmentation did not seriously degrade the size-selectivity of our measurements.

AlAr_n R.E.M.P.I. Spectra



Al Atom Absorption Spectrum in Ar Matrix



Abe and Kolb, *Ber. Bunsenges, Phys. Chem.* **87**, 523-527 (1983)

Figure 6

INTERPRETATION OF AlAr_n RESULTS

Comparison With Matrix Spectra

These spectra are compared to the UV spectrum of Al atoms trapped in an argon matrix^{8,9} in Figure 6. While the blue shifted peaks seen in the clusters are roughly in correspondence with the observed matrix bands assigned to the 3d state, the red-shifted bands observed in the cluster have no direct analog in the matrix spectrum. Indeed, the nearest band is further to the red but has been assigned to a significant (4200 cm^{-1}) red-shift of the lower 4s state.

The prominence of the red-shifted band and its continued shift to longer wavelengths with cluster size suggest that these spectra do not evolve directly to that of the matrix. Whetten and co-workers^{10,11} observed that the 4s band in AlAr_n clusters did blue shift as expected but towards an asymptotic threshold of 1700 cm^{-1} , far lower than the matrix value of 4200 cm^{-1} . The discrepancies between the spectra of larger clusters and the matrix spectrum provides vital information revealing how the intermolecular forces, either in the ground state or the excited state, perturb the electronic spectrum of the guest atom.

Comparison With Theory

Boatz and Sheehy (Phillips Laboratory, Edwards AFB) have performed Monte Carlo simulations attempting to model the spectra of AlAr_n clusters.^{12,13} These calculations make use of high level, large basis set MCSCF two-body potentials for ground and excited state AlAr recently calculated by Sheehy. Comparison with the calculations performed to date provide new insights into the differences between matrix and cluster spectra.

Classical Monte Carlo Simulations of AlAr_n Absorption Spectra - Balling and Wright Model

- Simulations Performed by Jerry Boatz - Phillips Laboratory, Edwards AFB
- AlAr Potentials Provided by Jeff Sheehy - Phillips Laboratory, Edwards AFB

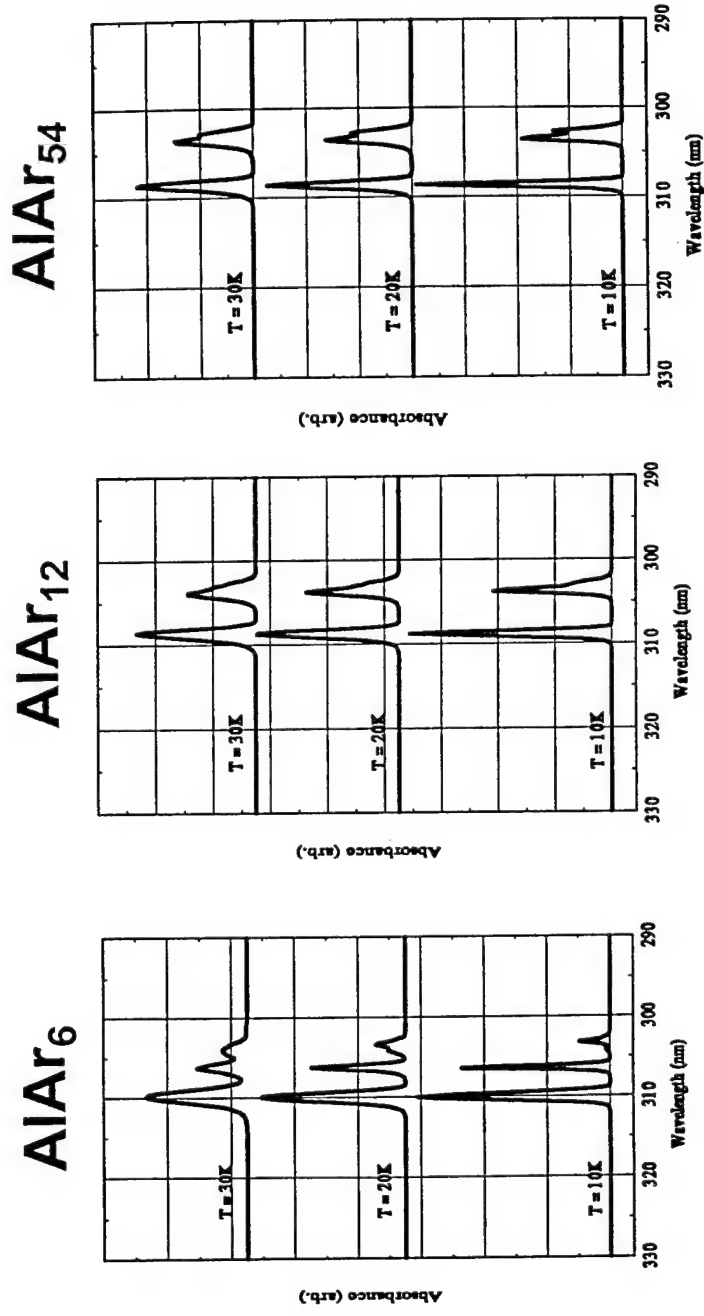


Figure 7

Figure 7 shows predicted Monte Carlo calculations within the Balling and Wright model.³ In this approximation, orbital orientation effects (i.e. mixing of the m_l levels of the 3d configuration) are considered in deriving adiabatic potentials. Many body effects and configuration mixing are neglected. As can be seen, the calculated spectrum qualitatively reproduces the splittings seen in the clusters. However, the red-shift of the longest wavelength band is significantly smaller than observed in the clusters and, furthermore, decreases with n rather than increasing. These discrepancies point to either many body effects or state-mixing as the origin of the large red-shifts seen in clusters. Such effects can be treated using more sophisticated methods such as the Spectral Theory of Langhoff.⁴

Predicted Cluster Structures

The cluster structures predicted by Boatz and Sheehy for $n = 6, 12,$ and 54 are shown in Figures 8 through 10. As can be seen, the Al atom sits at an apex of the icosahedron formed by the Ar atoms. This structure results from (1) the similarity of the Ar–Ar potential with the ground $X^2\Pi$ state Al–Ar when the singly occupied 3p orbital is perpendicular to the intermolecular axis, and (2) the repulsive nature of the interaction between Al and Ar when the 3p orbital is aligned along the intermolecular axis (the $A^2\Sigma$ state potential). The Al remains at a corner in order to minimize interaction between the occupied p orbital and the Ar atoms within the cluster.

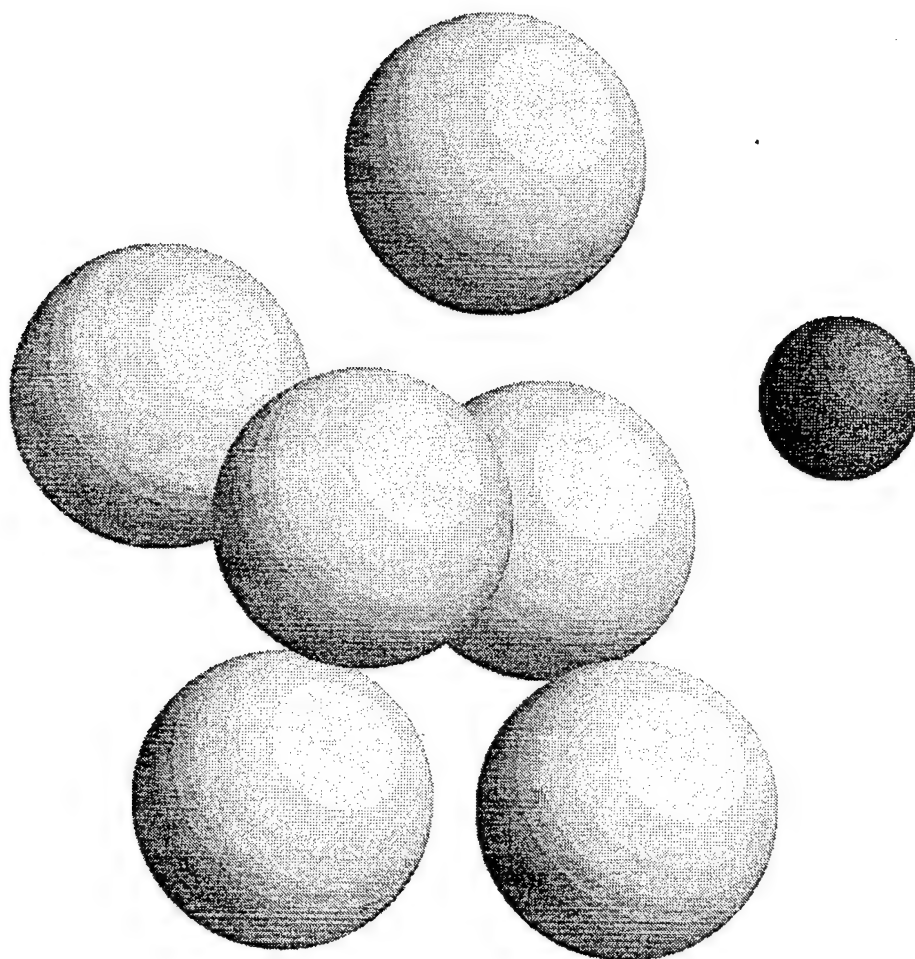


Figure 8

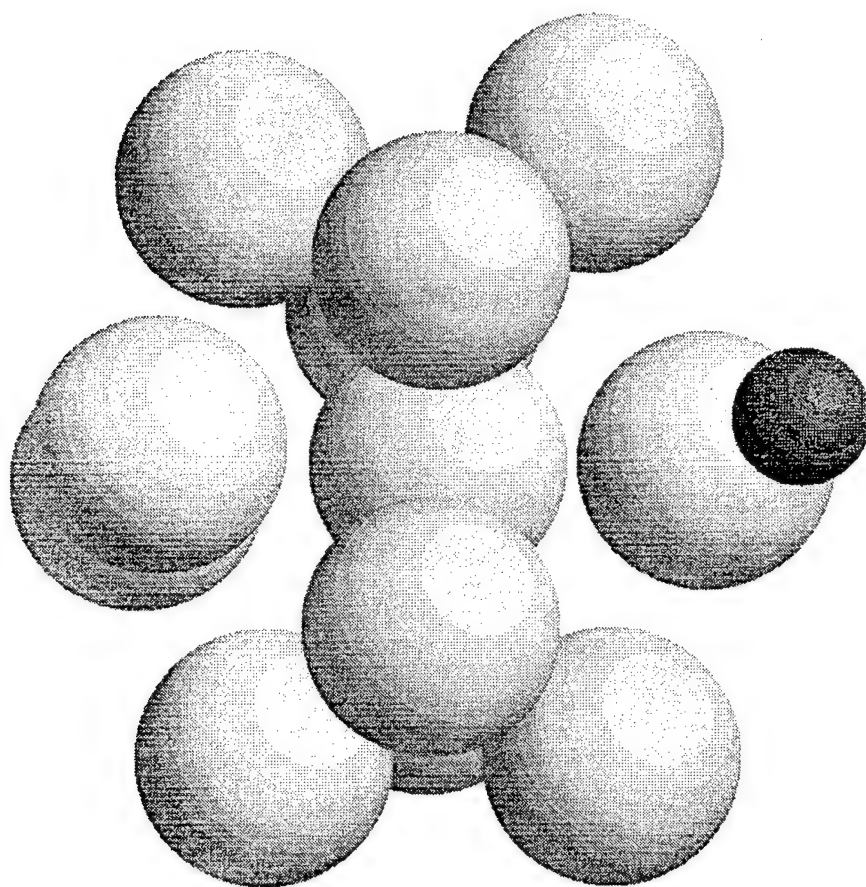
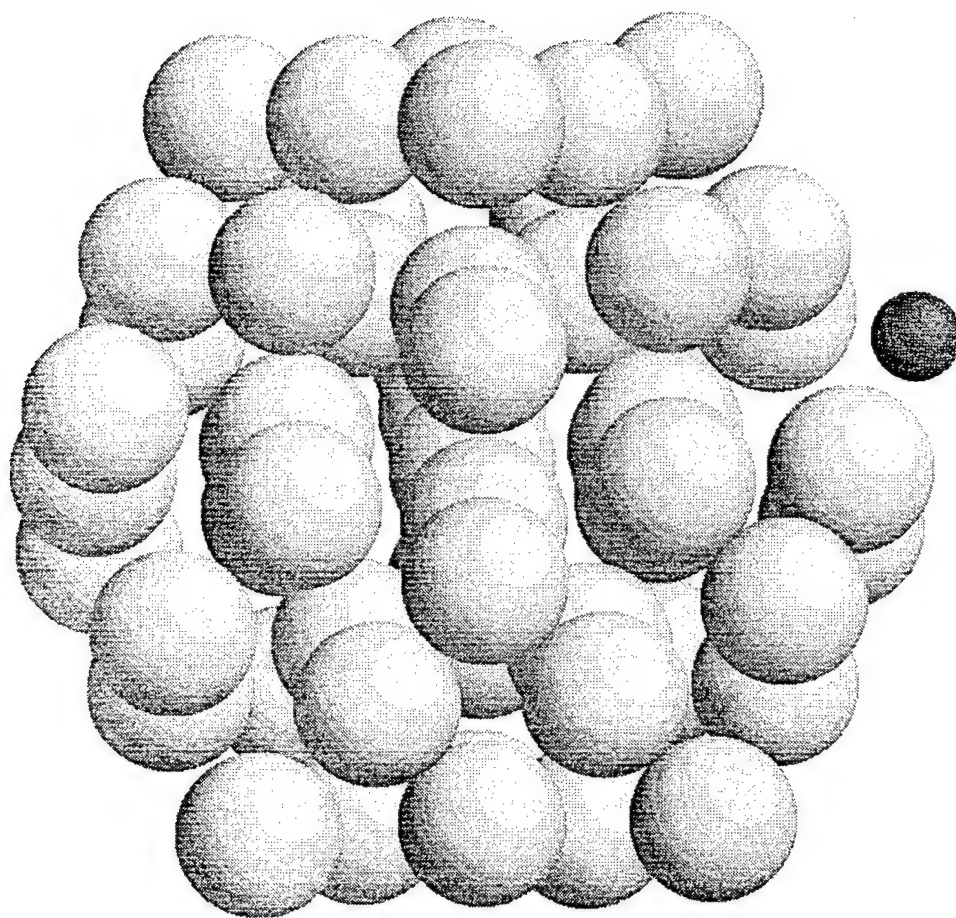


Figure 9.



AlAr₅₄

Figure 10

SPECTROSCOPY OF DIATOMIC AlAr

The model calculations being performed at Edwards AFB rely on accurate potential energy curves for Al-Ar in both the ground and excited electronic states. Sheehy has been calculating multi-reference CI calculations to obtain high quality ab initio potentials for diatomic AlAr. For the current studies, the potentials arising from the 3d and 4p Al atom states are particularly germane. Sheehy's potentials are shown in Figure 11. However, these states are poorly characterized spectroscopically. We therefore performed experiments to obtain vibronic spectra in the 300 nm region.

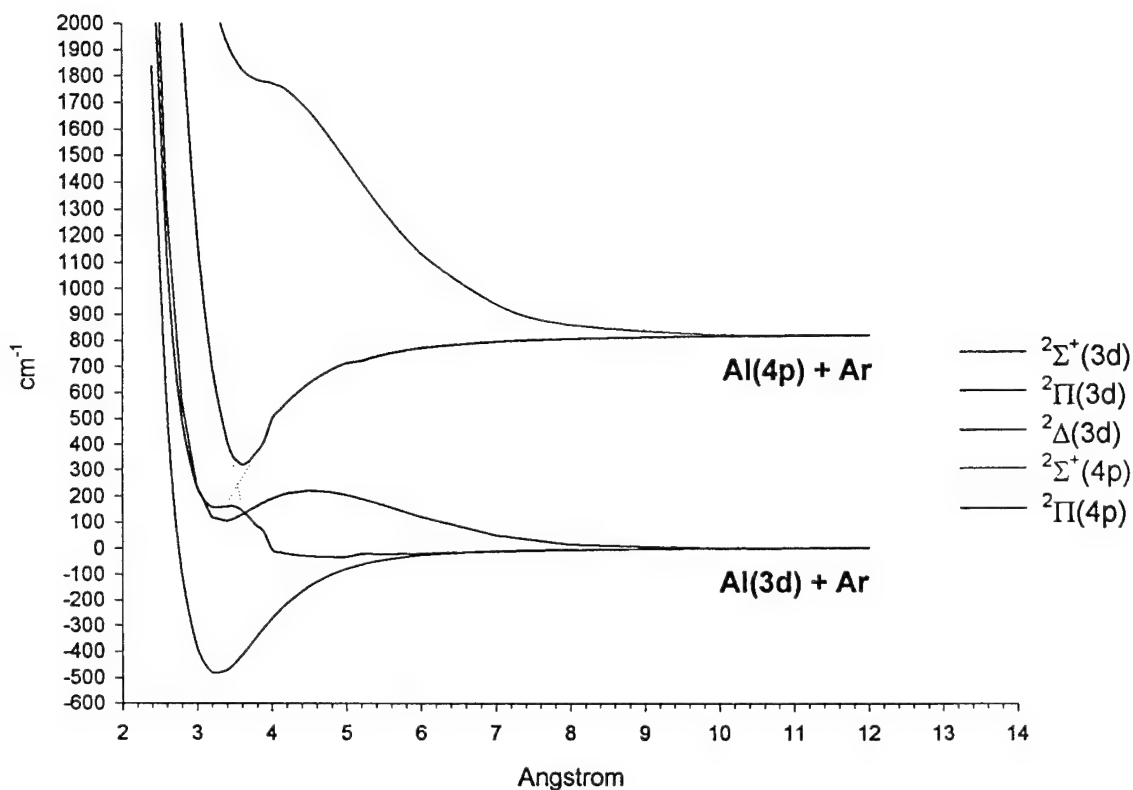
We have performed $1+1'$ and $2+1'$ resonant MPI spectroscopy of the diatomic molecule AlAr in order to re-examine the excited molecular states arising out of the 3d and 4p atomic states. These experiments probed states in the 33000 cm^{-1} region.

The two photon spectra represent new results. These spectra were taken because, in the isolated atom, the 3p-4p transition is a dipole-forbidden one-photon process, but is allowed for two photon excitation. Because the 4p state thus carries the two photon oscillator strength, these spectra represent excitation to molecular electronic states which possess an admixture of 4p character.

Spectra were detected in two ways: detection of the parent ion AlAr^+ , and detection of dissociation products Al^+ . Spectra recorded by the latter method are "action" spectra which result from excitation to predissociating (or directly dissociating) levels which form excited (3d or 4p) states of Al.

Al(3d)-Ar and Al(4p)-Ar Potential Energy Curves (MRCI from (6331) CASSCF (0.05) in Supplemented ANO Basis Set)

● Jeff Sheehy - Phillips Laboratory, Edwards AFB



- Key Points:**
1. Strong State Mixing Between $^2\Pi(3d)$ and $^2\Pi(4p)$
 - ♦ Calculated Energy Splitting = 151 cm^{-1}
 2. $^2\Sigma^+(3d)$ and $^2\Pi(4p)$ Cross - State Mixing?
 - ♦ Candidate for Perturbations above Nominal D_0
 3. $^2\Sigma^+(3d)$ has High Barrier - Bound Above D_0 ?
 4. Repulsive $^2\Sigma^+(4p)$ Potential
 5. $^2\Delta(3d)$ Mixes with $^2\Pi(3d)$ at High Vibrational Levels

Figure 11

AlAr 3d States: Single Photon UV Spectrum Below the Al(3d) Dissociation Limit

Single photon UV spectra (1+1') below the dissociation limit to the 3d state are shown in Figure 12. These spectra reproduce, with higher signal-to-noise and improved resolution, spectra taken by Morse and co-workers.¹⁴ Most notably, we observe two vibronic bands to the red of the previously observed progression assigned to the (3d)²Δ state. These bands fit the original progression and indicate that the literature value of the origin of this band is incorrect by approximately 135 cm⁻¹ too high. We find that $T_0 = 31895 \text{ cm}^{-1}$ for the (3d)²Δ state.

AlAr (4p) Mixing: Two Photon Spectrum Below the Al(3d) Dissociation Limit

Figure 13 presents a two photon spectrum of excitation to states in the same region as shown in Figure 12. While most of the bands are present, they possess significantly different intensities. Additional lines are present which do not appear in the one photon spectrum and are marked with an asterisk. These spectra, which have not yet been analyzed, provide a measure of mixing of the 3d and 4p states.

AlAr (4p) ²Π State: Two Photon Spectra Above the Al(3d) Dissociation Limit

The two photon spectrum recorded above the putative Al(3d) limit (shown in Figure 13) possesses a clear doublet progression which disappears at the Al(4p) dissociation asymptote. The spacing of the doublet is very close to the spin-orbit splitting in the 4p state of the Al atom. We therefore assign this progression to the (4p) ²Π state of AlAr.

These bands are absent in the single photon spectrum, indicating that these states have essentially no dipole oscillator strength to the ground state, i.e. little 3d, 4s, or 5s character.

The progression of doublets is observed in both the direct ionization and action channels. The observation of this progression by action spectroscopy indicates that this state predissociates efficiently but not entirely to Al(3d) on the timescale of the laser pulse. The differences between the two channels are evidence for state-specific predissociation dynamics. Most notably is a broadening of one component ($\Omega = 1/2$) of each pair of bands near 32600 cm^{-1} , which we attribute to curve crossing by the $(3d)^2\Sigma^+_{1/2}$ state.

AlAr (4p) $^2\Sigma^+$ State: Two Photon Spectra Above the Al(4p) Dissociation Limit

Based on Sheehy's *ab initio* prediction for the location of the repulsive $(4p)^2\Sigma^+$ state, we scanned the two photon action spectrum in the region above the Al(4p) + Ar dissociation limit. We observed the broad, asymmetric band shown in Figure 14 and assigned it to the previously unobserved $(4p)^2\Sigma^+_{1/2}$ state. The width and near absence of this peak in the AlAr⁺ channel confirm the dissociative nature of this band. The overall shape should be a good test of the shape of the potential and the nature of the transition dipole function predicted by theory.

Al(3d,4p)-Ar \leftarrow Al(3p)-Ar Transitions $1\nu_{UV} + 1\nu_{vis}$ R.E.M.P.I.

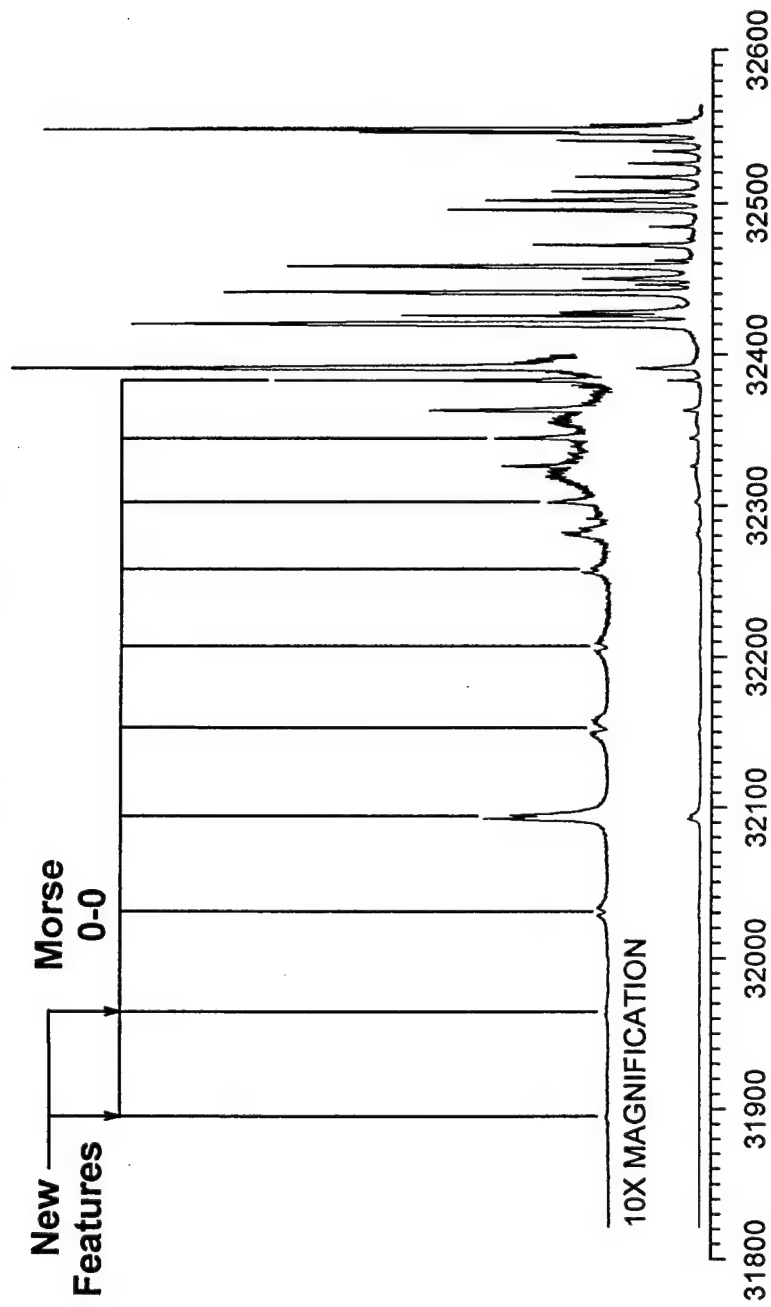
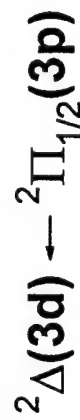


Figure 12

Comparison Between Single vs. Double Photon Excitation on AlAr^+ Signal

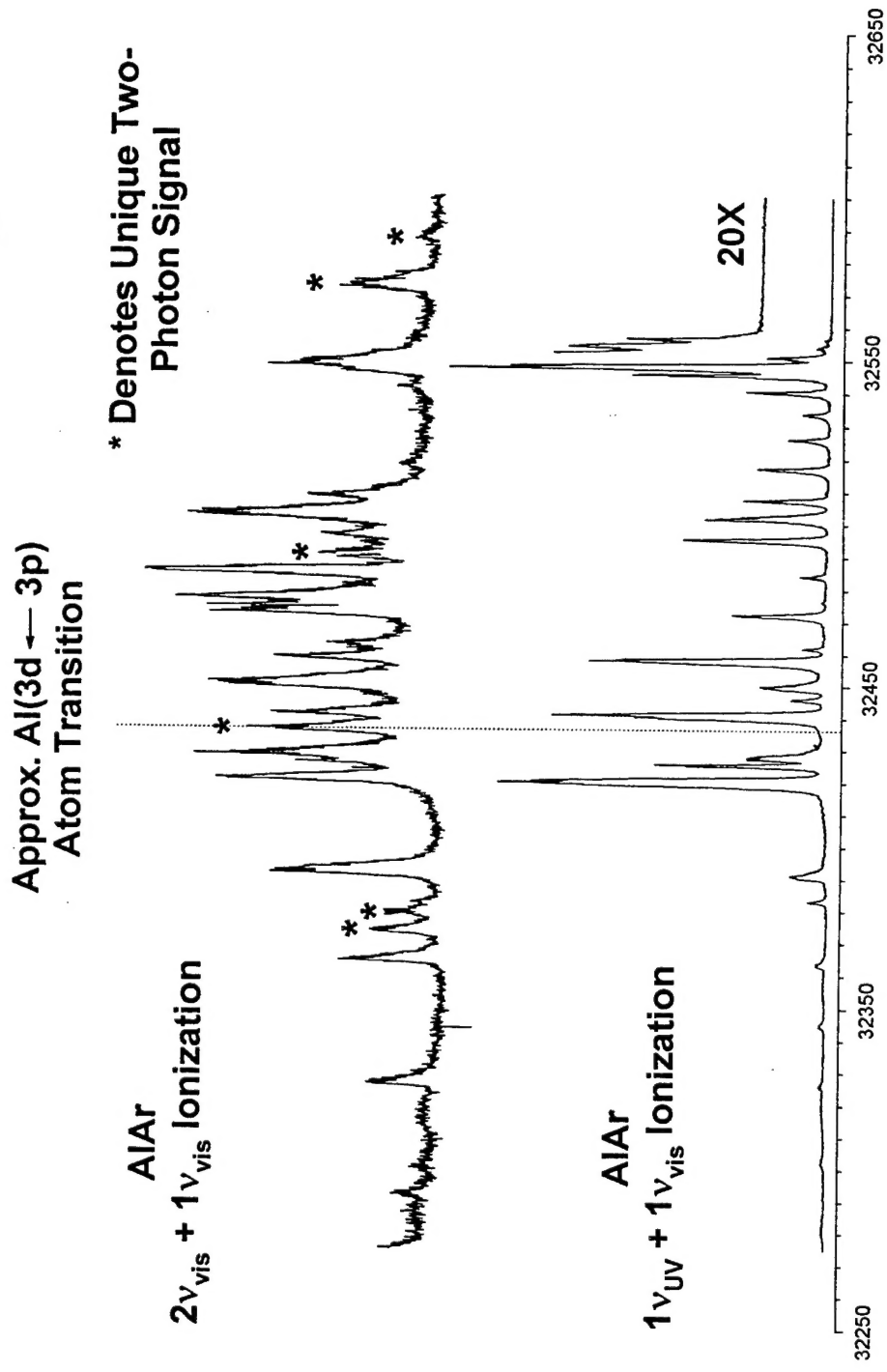


Figure 13

AlAr and Al Fragments above Morse Al(3d)-Ar D₀

$2\nu_{\text{vis}} + 1\nu_{\text{vis}}$ R.E.M.P.I.

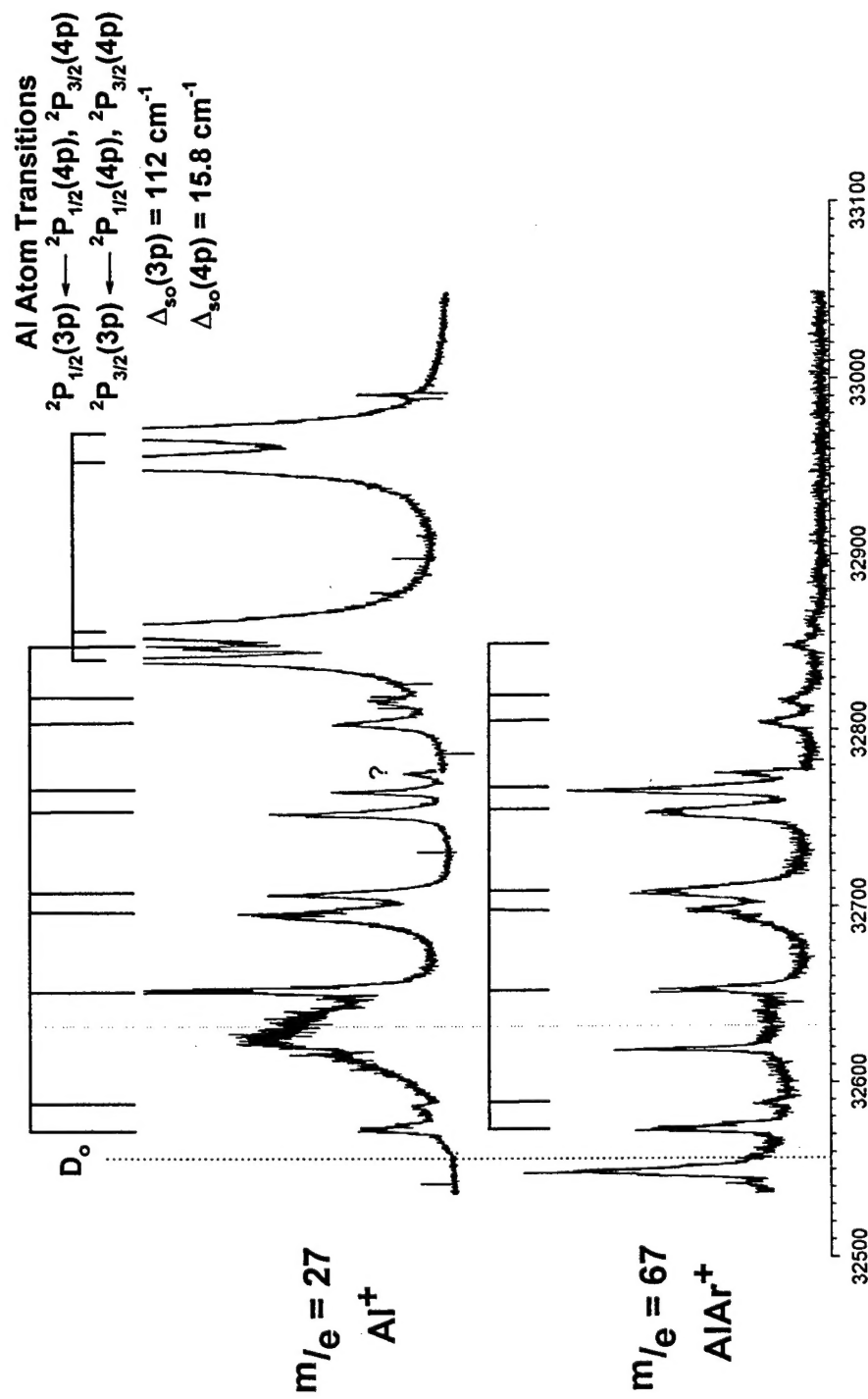
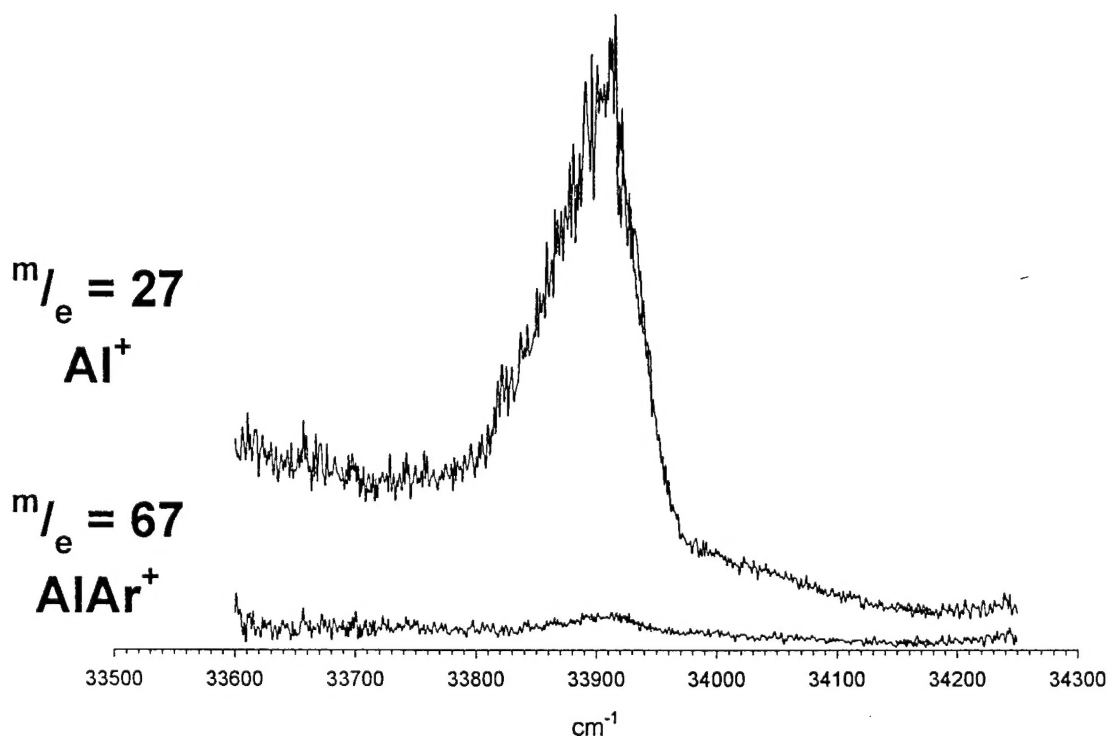


Figure 14

Evidence for $^2\Sigma^+$ (4p) State in AlAr



- ♦ Strong Al Atom Signal
- ♦ $^2\Sigma^+$ (4p) Potential Appears Repulsive at Ground State r_e Distance of 4 Angstroms
- ♦ Theoretical Potential Curves Predict Interesting Curvature in This Region

Figure 15

REFERENCES

-
- ¹ *Proceedings of the High Energy Density Materials (HEDM) Conference*, edited by P. G. Carrick and S. Tam (Phillips Laboratory, Edwards AFB, CA, 1996).
- ² M. E. Fajardo, S. Tam, T. L. Thompson and M. E. Cordonnier, *Chem. Phys.*, **189**, 351-365 (1994); J. A. Boatz and M. E. Fajardo, *J. Chem. Phys.*, **101**, 3472-3487 (1994); R. A. Corbin and M. E. Fajardo, *J. Chem. Phys.*, **101**, 2678-2683 (1994); S. Tam and M. E. Fajardo, *J. Chem. Phys.*, **99**, 854-860 (1993); M. E. Fajardo, *J. Chem. Phys.*, **98**, 119-125 (1993); M. E. Fajardo, *J. Chem. Phys.*, **98**, 110-118 (1993); M. E. Fajardo, P. G. Carrick and J. W. Kenney, *J. Chem. Phys.*, **94**, 5182-5825 (1991).
- ³ L. C. Balling and J. J. Wright, *J. Chem. Phys.* **79**, 2941 (1983).
- ⁴ P. W. Langhoff, *J. Phys. Chem.*, **100**, 2974-2984 (1996).
- ⁵ W. C. Wiley and I. H. McLaren, *Rev. Sci. Instrum.* **26**, 1150 (1955).
- ⁶ D. Proch and T. Trichl, *Rev. Sci. Instrum.* **60**, 713 (1989).
- ⁷ R. E. Continetti, Ph.D. Thesis, University of California, Berkeley, CA, 1989.
- ⁸ H. Abe and D. M. Kolb, *Ber. Bunsenges. Phys. Chem.*, **87**, 523-527 (1983).
- ⁹ R. Grinter and R. J. Singer, *Chem. Phys.*, **113**, 87-97 (1987).
- ¹⁰ R. L. Whetten, K. E. Schriver, J. L. Persson and M. Y. Hahn, *J. Chem. Soc. Faraday Trans.*, **86**, 2375-2385 (1990).
- ¹¹ K. E. Schriver, M. Y. Hahn, J. L. Persson, M. E. LaVilla and R. L. Whetten, *J. Phys. Chem.* **93**, 2869-2871 (1989).
- ¹² J. A. Boatz and J. Sheehy, private communication.
- ¹³ J. A. Boatz and J. A. Sheehy, Extended Abstract, 1997 HEDM Contractor's Meeting, Chantilly, Virginia, June 1997.
- ¹⁴ S. A. Heidecke, Z. Fu, J. R. Colt, and M. D. Morse, *J. Chem. Phys.* **97**, 1692 (1992).